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14. ABSTRACT

This report details the work performed on the project, "Novel Material Designs To Enable fabrication of High Quality, Affordable, and Performance Consistent Phase Shifters For OTM Phased Array Antennas" during the period, July 2007 to February 2012. It contains an overview and background of the project and describes our technical progress, challenges, and important results.
The report also discusses our collaboration with ARL and the transfer of MOCVD film growth technology from

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Report Title

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The report also discusses our collaboration with ARL and the transfer of MOCVD film growth technology from Caltech to ARL.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
2011/09/01 0: 1	M. W. Cole, D. A. Boyd. Growth of Compositionally Graded BST by Metal Organic Chemical Vapor Deposition, Integrated Ferroelectrics, (01 2011): 0. doi: 10.1080/10584587.2011.574970

TOTAL: **1**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

  TOTAL:

Number of Manuscripts:

Books

Received   Paper

  TOTAL:

Patents Submitted

Patents Awarded

Awards

Chosen by the National Academy of Engineering (NAE) to participate in its 16th annual U.S. Frontiers of Engineering symposium. The event be September 23-25 at the IBM Learning Center in Armonk, New York, brings together 87 engineers ages 30 to 45 "who are performing exceptional engineering research and technical work in a variety of disciplines" and are considered by NAE to be among "the nation's brightest."

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David A. Boyd	0.47	
FTE Equivalent:	**0.47**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report for Proposal Number 49731EL, *Uniform-large Area BaSrTiO₃ Growth and Novel Material Designs To Enable fabrication of High Quality, Affordable, and Performance Consistent Phase Shifters For OTM Phased Array Antennas*

David A. Boyd
Caltech

July 11, 2012

Abstract

This report details the work performed on the project, *Novel Material Designs To Enable fabrication of High Quality, Affordable, and Performance Consistent Phase Shifters For OTM Phased Array Antennas* during the period, July 2007 to February 2012. It contains an overview and background of the project and describes our technical progress, challenges, and important results. The report also discusses our collaboration with ARL and the transfer of MOCVD film growth technology from Caltech to ARL.

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I   Introduction

This report details the work performed on the project, *Novel Material Designs To Enable fabrication of High Quality, Affordable, and Performance Consistent Phase Shifters For OTM Phased Array Antennas* during the period, July 2007 to February 2012. The report contains an overview and background of the project, our technical progress, and a discussion of our collaboration with ARL.

II   Statement of the Problem

The motivation for this project was to develop a fabrication process that can reproducibly grow high quality BST thin films and thin film heterostructures with good control of material properties over large area substrates. The intended use of the films is in phase shifters for electronically scanned phased array antennas (ESAs). The criteria for the film growth method are 1) meet the affordability compliance and 2) mitigate the performance inconsistency. Large area films provide economies of scale. Uniform materials properties across the wafer and from wafer to wafer are necessary for devices that have consistent performance. Thin film heterostructures, e.g. graded films, can provide a cost-effective method to compensate for thermal changes in the dielectric properties of the materials, which can adversely alter the performance of ESAs.

i   Background

The metal organic chemical vapor deposition [MOCVD] technique was chosen because it is the only film growth method that can reliably meet both of these competing criteria. MOCVD is an industry standard growth tool in both the semiconductor and microelectronics industries. It provides precise control of film thickness with large area compositional uniformity, possesses high deposition rates, and enables wafer-to-wafer repeatability. MOCVD is a cost-efficient and scalable technique for a wide range of materials.

MOCVD involves exposing a heated substrate to flow of metalorganic chemical precursors that react with the substrate and deposit a film. At room temperature, the metalorganic precursors are solid phase and must be heated to achieve a suitable vapor pressure. The precursors are contained in hermetic "bubblers" that are in turn housed in an oven. The ovens are heated, and a gas such as argon flows into the bubbler and carriers the vaporized precursor molecules to the substrate. The precursors decompose and react in a controlled manner at the substrate, which is heated to hundreds of degrees Celsius, to continuously deposit a thin film. For oxides, a flow of oxygen is present.

A challenge with multi-components films and film structures is achieving and maintaining stoichiometry film throughout the growth run. For a single component film e.g. TiO_2, the precursor flux can be determined from the known vapor pressure of the precursor and the mass flow of the carrier gas. It is not usually necessary to the monitor and or control the flux since changes in the vapor pressure of the precursor typically will only affect the instantaneous growth rate and not the overall composition of the film. However, for multi-component films, e.g. BST, the relative amount of each component must be controlled throughout the growth run. Control is also needed because there are a number of factors affecting the precursors flux including bubbler oven temperature drift, precursor decomposition, and performance variability of the precursors. Control of the precursor flux is absolutely necessary for the growth of more

complicated film structures such as compositionally graded films because the relative amounts of each precursor must be varied with time.

A unique feature of the Caltech reactor system is that each component of the precursor flux can be controlled in real-time. The control is based on real-time absorption measurements of the vaporized precursors before they reach substrate. Each of the MOCVD precursors use absorbs light in the UV, and each of the bubblers has an in-line UV optical cells where the strength of the absorption is measured in real-time. Using the Beer-Lambert law and knowledge the measured flow of carrier gases, temperature, and pressure, one can determine the molar flux of each precursor entering the reactor. The molar fluxes for Ba, Sr, and Ti are measured and computed in real-time, and these measured values are then used as control points in a PID control loop for each precursor source. The total amount of precursor reaching the sample is determined by the flow of the carrier gas, which is controlled by an electronic mass flow controller (MFC) dedicated to each precursor source. These control loop allows control of the relative amounts of Ba, Sr, and Ti, and the overall total mass flow in umole/min reaching the substrate. In all, there are three independent control loops. This approach has worked very well for the Caltech reactor and has allowed us to grow multi-component oxide films including YBCO and ferroelectric PBT. In this project, we applied this precursor control technology to creating BST thin films and thin film structures.

III   Technical Achievements

i   Software

The reactor control code (RCC) controls and monitors all aspects of the MOCVD film growth. The original RCC, RCC 1.0, previously developed by Caltech was not capable of creating the complex film structures needed for this project. This code allowed only for constant composition films to be grown. Once a particular set of molar ratios were chosen, they could not be systematically changed during the growth. RCC 1.0 would thereby not allow compositionally graded heterostructures or any complex heterostructures. Furthermore, this original code was DOS based and did not have a GUI for visually monitoring critical data with time.

In the first year of this project, an entirely new code, RCC 2.0, was developed. This work was performed in collaboration with Melanie Cole of ARL, as will be discussed later. RCC 2.0 has a number of advances and features. The key feature of this RCC is the ability to arbitrarily change the molar ratios of the precursor flux and as well all other growth parameters during the growth run process. For example, films can be prescribed to include gradients, steps, and or periodic variations in composition. This control code allows us to create growth recipes as well as a great deal of flexibility for us to modify the process parameters such as total flow rates and substrate temperature. In addition, RCC 2.0 is based on hardware real-time control that is independent of the Windows OS. This alleviates many of the problems caused by the instability of the Windows OS. A system crash during growth can not only stop the growth, it can cause damage to the reactor hardware, e.g. the sample heater. If the computer running the interface crashes in our current system, the process hardware can still continue to control the process. RCC 2.0 also features a full GUI and monitoring of all the process parameters including multiple process temperature, pressure, heater power, and mass flows. The GUI for UV spectral collection and control window allows us to monitor the entire UV spectra in real-time, which has been very useful in determining control setpoints and monitoring
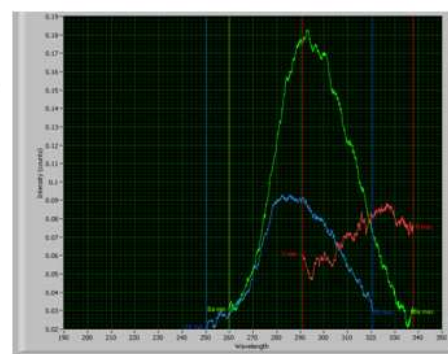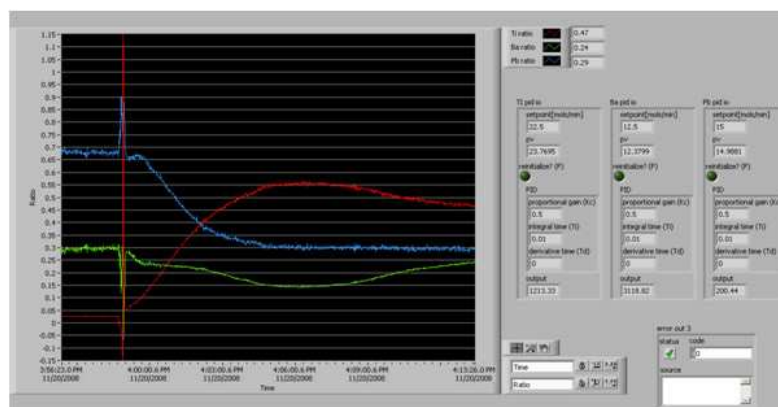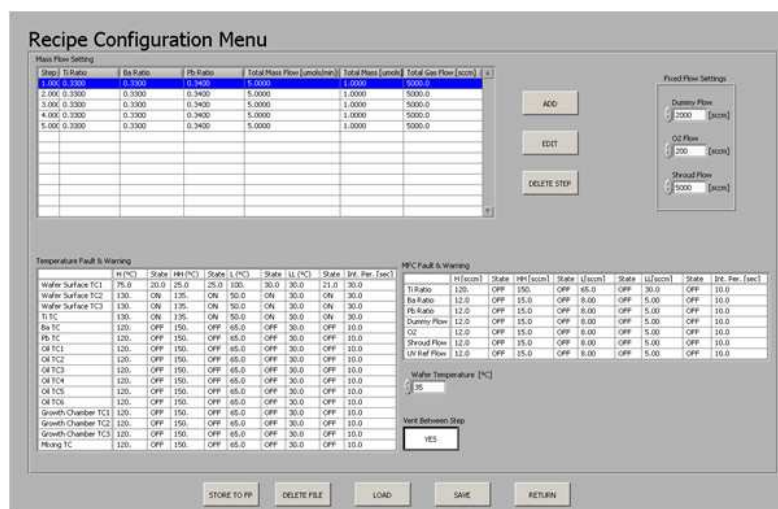
Figure 1: Images from the RCC 2.0. Recipe Menu, top left; LabView Fieldpoint real-time controller, top right; UV Spectral Menu, showing all three absorptions of the precursor flux in real time, bottom right; Molar Ratio Menu showing the relative amounts of the three precursors components in real time, bottom left.

the precursor delivery system. Shown in Figure 1 of the attached file are screen shots of the LabView Fieldpoint real-time controller, the Recipe Menu of the RCC, which allows a user to prescribe all the parameters of the film growth, and the Precursor Ratio Menu, which shows the real-time measurements of the precursor flux. RCC 2.0 is written in LabView and has been designed to be ported to the MOCVD reactor system ARL has constructed, as will be discussed later.

RCC 2.0 allows for two modes of operation: manual and automatic. The manual mode allows for individual control of all the setpoints such as substrate temperature, molar ratios, total mass flow, etc, at any time of the deposition process. This is useful for process development. The manual mode has four independent control loops (one for the sample heater and three for the precursor delivery), separate independent routines for saving parameters, independent relay control, a pressure control loop, a timed loop for the PID control UV ratio control, and a timed, secondary loop, nested state machine to switch between manual, auto, and idle states. In manual mode everything is controlled on the client side, and this mode is suited for exploring the process parameter space, testing setpoints, and growing films with a constant stoichiometry. The code is top level is controlled by an event structure, where the client, i.e. the host computer,

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sends commands to the real-time hardware controller. In the automatic mode, all aspects are controlled from the LabView Fieldpoint hardware controller (real-time processor). The entire growth process is driven by a recipe of setpoint values. The automatic mode has independent control loops, (no state machines), a small loop to event logging, routines for handshaking between the client and real-time processor. In both the manual and automatic modes, the real-time controller has independent control loops for the pressure and the heater controller, data logging, a timed control loop for the UV-precursor control.

Qualification of RCC 2.0 was started in the Fall of 2008 with films of constant composition. The MOCVD reactor is a complex system, and we anticipated, as in any such project, that minor software and hardware issues would arise under actual working reactors conditions and need and to be resolved. In particular, the integrity of the hardware/sofware communications, PID control system parameters, memory management and behavior of fault conditions needed to be established. For example, testing and determination of the PID control parameters of the precursor delivery systems required that the MOCVD bubbler and all the gas lines leading to the reactor to be heated to working temperature. Testing and qualification of RCC 2.0 was performed during the second year of this project. Major issues with software architecture and hardware interface were encountered and resolved. Successful growth of *constant* composition films were obtained over a range of desired stoichiometries (described in the next section).

Testing and qualification of RCC 2.0 for *graded and complex* films began in the summer of 2009. The process architecture for film growth in the automatic mode is a series of steps. For each step, there is a particular state of conditions, and the step is complete when a prescribed amount of mass has reached the sample. The state conditions include the precursor ratios, mass flow rates, and total flow rate. The total mass reaching the substrate during the step is determined from the UV and flow measurements. An arbitrary number of steps can be stitched together to create a desired heterostructure. Shown in Figure 2 is a screen shot of the recipe tab showing a recipe for growth of a five layer heterostructure.

During testing and development of the automatic mode, it was realized that the transition between the individual steps of the recipe was an important consideration. This is because of the relatively long time constants of the overall system. The time constant of the precursor delivery system is largely determined by the volatility of the precursors themselves, and this can vary for each. Typically, the response time to changes in flow stoichiometries are realized in tens of seconds, and the time to reach the desired setpoint will depend on the severity of the requested composition change. For continuously graded materials, gas composition changes between steps are small and the steps can blend into one another. However, when more dramatic steps are required, e.g. a TiO_2 layer on 60:40 BST, a continuous transition cannot be used because the time between steps would not allow for sharp stoichiometric transition to occur. Changes in substrate temperate behave in a similar temporal manner.

To overcome the issue of transitions, a fault control system was developed. Simply stated, a recipe step would begin only when the conditions were within specified limits of the desire composition and temperature. Otherwise the precursor flux was automatically vented away from the sample until the conditions were met. Shown in the lower portion of Figure 2 are the temperature and flow fault warnings used in the recipe configuration.

An additional issue that was addressed relates to the chamber pressure between steps. It is highly desirable to maintain a constant pressure in the chamber, and simply stopping the precursor flux would result in a large pressure disturbance. To avoid this, when the precursor flow is vented, it is immediately replace with dummy flow nitrogen of the exact same magnitude.

Recipe Configuration Menu

Mass Flow Setting

Step	Ti Ratio	Ba Ratio	Pb Ratio	Total Mass Flow [umols/min]	Total Mass [umols]	Total Gas Flow [sccm]
1.000	0.3300	0.3300	0.3400	5.0000	1.0000	5000.0
2.000	0.3300	0.3300	0.3400	5.0000	1.0000	5000.0
3.000	0.3300	0.3300	0.3400	5.0000	1.0000	5000.0
4.000	0.3300	0.3300	0.3400	5.0000	1.0000	5000.0
5.000	0.3300	0.3300	0.3400	5.0000	1.0000	5000.0

ADD   EDIT   DELETE STEP

Fixed Flow Settings
Dummy Flow 2000 [sccm]
O2 Flow 200 [sccm]
Shroud Flow 5000 [sccm]

Temperature Fault & Warning

	H (°C)	State	HH (°C)	State	L (°C)	State	LL (°C)	State	Int. Per. [sec]
Wafer Surface TC1	75.0	20.0	25.0	25.0	100.	30.0	30.0	21.0	30.0
Wafer Surface TC2	130.	ON	135.	ON	50.0	ON	30.0	ON	30.0
Wafer Surface TC3	130.	ON	135.	ON	50.0	ON	30.0	ON	30.0
Ti TC	130.	ON	135.	ON	50.0	ON	30.0	ON	30.0
Ba TC	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Pb TC	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC1	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC2	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC3	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC4	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC5	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Oil TC6	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Growth Chamber TC1	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Growth Chamber TC2	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Growth Chamber TC3	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Mixing TC	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0

MFC Fault & Warning

	H [sccm]	State	HH [sccm]	State	LL [sccm]	State	LL [sccm]	State	Int. Per. [sec]
Ti Ratio	120.	OFF	150.	OFF	65.0	OFF	30.0	OFF	10.0
Ba Ratio	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0
Pb Ratio	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0
Dummy Flow	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0
O2	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0
Shroud Flow	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0
UV Ref Flow	12.0	OFF	15.0	OFF	8.00	OFF	5.00	OFF	10.0

Wafer Temperature [°C] 35

Vent Between Step YES

STORE TO FP   DELETE FILE   LOAD   SAVE   RETURN

Figure 2: A screen shot from RCC 2.0 showing the recipe tab for graded depositions. The process parameters for each step can be prescribed including substrate temperature, film stoichiometry, and total mass flow rate.

Although the ability to switch between vent and run flows has always been part of the system, it was not part of the control loop and more importantly the switching was not refined enough to prevent pressure rises. The switching involves two valves that were switched simultaneously, and it was found by allowing them to switch in a timed sequence, we could avoid most of the disruption in the pressure during switching.

Modifications were made to the RCC to improve the UV spectral integrity. In longer runs, we began to experience a drift in the UV control signals with time, and this could adversely affect control. The heart of the UV control of the precursor delivery system is the deuterium lamp, and an issue we were having is drifting of the lamp during the run. This is a problem because the absorbance signal is measured relative to a reference spectrum taken when there is no precursor vapor present i.e. the bubblers are closed. If the lamp signal drifts, this results in false change in the absorbance. To overcome this, we developed a variable that is called the lamp drift factor (LDF). The current output spectrum of the lamp is compared to that taken at the time of reference. Changes in the lamp spectra are assumed to affect the three control channel equally, and the reference spectrum for each channel is modified by the LDF. Shown in Figure is a screen shot of the LDF. For zero drift, the signal will remain at unity. Figure 3 shows how the LDF has changed after approximately one hour after starting the lamp.

Further improvements were made in UV spectral processing with the addition of signal averaging. In any spectrometer there is tradeoff between signal intensity and collection time: longer collection times allow for improved signal to noise. When using a spectrometer as part of control system, longer collection times result in less responsive system control. To strike a balance, we implemented a variety of signal processing options in the RCC to improve the UV control stability. In particular, signal averaging has been included and this has resulted in improved process control. Shown in Figure 4 is a screen shot of the signal averaging options. The averaging options include vector averaging, RMS averaging, and peak hold. The weighting
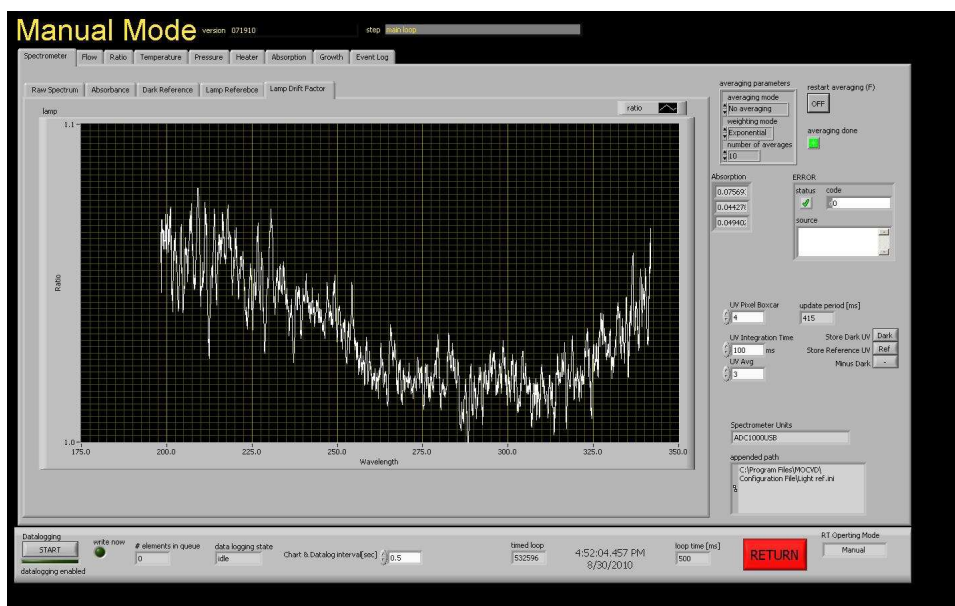
Figure 3: A screen shot of the RCC 2.0 showing the lamp drift factor one hour after starting the lamp.

mode allows for linear and exponential, and there is an number of signals to average can be selected as well.

ii   Film Growth

As with any new MOCVD process, the exact BST process parameters had to be determined empirically. The control of the precursor flux in the Caltech MOCVD system is dependent on the vapor pressure and the UV absorption features of the metalorganic precursors, and to date these values for Sr had not been measured nor were they available in the literature. The first practical issues that had to be determined was the operating temperature of the Sr bubbler and the UV spectral absorption window that would be used for control. Although we can carefully control the precursor flux reaching the sample, the final film composition will depend on the relative reactivity of the precursor, which can vary between manufacturers and lots. The overall BST reaction kinetics would also have to be determined.

A series of MOCVD growth runs were used to determine the properties of the strontium precursor and the kinetics of the metalorganic BST system. Constant composition runs were performed to study the reactor system itself and the behavior of the precursors as well as establish the integrity of the hardware and software. The internal milestones for the initial BST growth runs were as follows: 1) establishing the integrity of the control software and hardware by testing under growth conditions, 2) determine the PID parameters for the real-time precursor delivery system , 3) determine the PID parameters for the substrate heater, 4) measurement the UV absorbance spectrum for the Sr(thd) precursor and determine the wavelength spectral window for control, 5) determination of the Sr bubbler temperature, and 6) empirically determine the molar precursor ratios required for a BST (Ba:Sr, 60:40) film. Given that the RCC and hardware performed satisfactorily, the composition of the films would be analyzed, and this data would to be used adjust the molar ratios in subsequent growth runs.

BST growth runs of constant composition began in the Fall of 2008. Based on our pre-

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Figure 4: A screen shot of the RCC 2.0 showing signal averaging options (red circle) for processing the UV absorption

vious work with oxides, sample temperature was set to nominally 600 °C, the total pressure was 15 Torr, and a 2 slm flow of oxygen was present. The total mass flow was nominally 1 umol/min. The basic growth conditions are summarized in Figure 5. The metal organic precursors were a) titanium: Bis(isopropoxy)bis(2,2,6,6-tetramethylheptane-3,5-dionato)titanium b) strontium: Bis(2,2,6,6-tetramethylheptane-3,5-dionato)strontium aka $Sr(THD)_2$, and c) barium: Bis(2,2,6,6-tetramethylheptane-3,5-dionato)barium, aka $Ba(THD)_2$. The precursor ratios were chosen to be stoichiometric. 30:20:50 (60:40) BST. Sample substrates were MgO, Si+Pt, Si, and Al_2O_3 (sapphire) one of each was included per run. We determined that the operating temperature for the Sr(thd) precursor was between 232 and 235 °C, and that the absorption window for Sr was is 250-320 nm. These values are also summarized in Figure 5

A series of growth runs was performed with the goal of establishing the BST growth pa-

T_{growth} (C)	Ba/(Ba+Sr+Ti)	Sr/(Ba+Sr+Ti)	Ti/(Ba+Sr+Ti)	Pback (Torr)	Total Mass Flow (µmole/min)	Flow O2 (slm)	Carrier Gas
600	0.3	0.2	0.5	15	1	2	Ar

Precursor	T bubbler (C)	UV Spectral Window (nm)
Ba	237	260-335
Sr	232-235	250-320
Ti	135-140	290-335

Figure 5: A summary of basic BST growth conditions, bubbler temperature, and UV spectral control windows.

rameters. After each run, the composition and microstructure of the films was examined. ARL assisted in the characterization of the films, which included XRD and RBS. These result provided feedback for the subsequent growth run. Characterization of the first two runs revealed a layer of titania had formed before the BST layer. This was unusual. The problem was explored, and it was found that a faulty control valve had erroneously allowed precursor to reach the sample instead of being vented. The issue with the valve was resolved. A software control issue was also encountered and corrected.

This series of growth runs continued and was able to produce good quality BST film.[1] Films were simultaneously grown on Si, Si/Pt, Al_2O_3, and MgO substrates. Shown in Figure 6 and Figure 7 are characterizations of an exemplar run that produced BST 80:20. Figure 6 provides the growth conditions and shows a SEM cross-sectional image of a 70 nm BST film on a Pt/Si (electroded) wafter. (Note that a 40 nm layer of sputtered Ti was used as an adhesion layer between silicon and platinum.) The SEM image shows good layer delineation. Figure 7 are x-ray diffraction (XRD) measurements of BST grown on sapphire, silicon, magnesium oxide and platinum on silicon. These measurements show that the films on Si, Si/Pt, MgO, and Al_2O_3 are crystalline BST with a preferred (110) orientation. Small amounts of (111) and (211) phases were present.

From this series of runs, we determined the growth conditions to produce BST films over a range of Ba:Sr ratios. The ratios achieved spanned nearly the entire range of composition desired for compositionally graded films. For example, the desired "up-graded" films would range in composition from (Ba:Sr) 30:70 to 90:10. These growths runs also provided us the bounding values of the growth rates to the control recipe. The Ba precursor was found to have the lowest reactivity of the three components, and it limits the growth rate of the film. As an example, layers with low barium will be able to grow faster than those with high amounts of barium. We note that all the substrates, MgO, Al_2O_3, Si, and Si/Pt, in each run were subjected to exactly the same precursor fluxes for a given run, but we observed that the film compositions can vary for each substrate.

Having determined the necessary growth parameters for constant composition BST, the next goal was to establish the capability of the RCC 2.0 to create complex films structures. The first set of runs verified that the RCC 2.0 was satisfactory for control of constant composition films. The architecture of RCC 2.0 was established during testing; it performed all tasks as required, and the major bugs had been worked out. The code modifications to create complex heterostructures were then put in place, and testing this aspect of the code was begun. A notable improvement in the code was the ability to work with to simulated UV absorption signals. This provided a great time saving as much of the RCC could be tested without the need for heating the precursors.

In the third year of this project, we were able to demonstrate controlled growth of compositionally stratified BST films by MOCVD.[2] As an example, we were able to create an "up" graded BST film using a five step recipe. The conditions were as follows. The Ti precursor flow ratio was held constant at 0.22 for each of the steps; the Ba precursor flow ratio varied from 0.37, 0.47, 0.57, 0.67, and 0.77; and the Sr was correspondingly 0.41, 0.31, 0.21, 0.11, and 0.01. The total mass for each step was 10 μmole. Based on our previous work with oxides, sample temperature was set to nominally 600 °C, the total pressure was 15 Torr, and a 2 slm flow of oxygen was present. The total mass flow was nominally 1 umol/min. The substrates used were Si, Si/ Pt (electroded), sapphire, and MgO.

Rutherford backscattering spectroscopy (RBS) was used to characterize the composition of

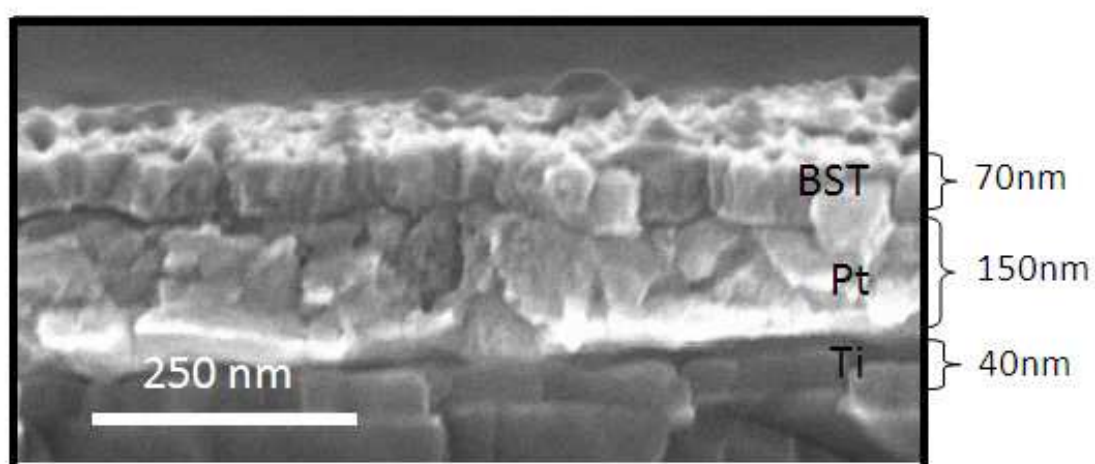| Run 6: Ratio Setpoint	MgO	Sapphire	Si	Si+Pt (spotty)
Ba=0.61	0.443	0.363	0.565	0.448
Sr=0.17	0.130	0.143	0	0.109
Ti=0.22	0.427	0.493	0.435	0.443
(Ba+Sr):Ti	1.26	1.75	0.77	1.23
Ba:Sr	77:23	72:28	100:0	80:20

Figure 6: A summary of molar flow ratios and composition values, as measured by EDS, top. SEM cross-section of a resulting BST film on Pt-Ti-Si.
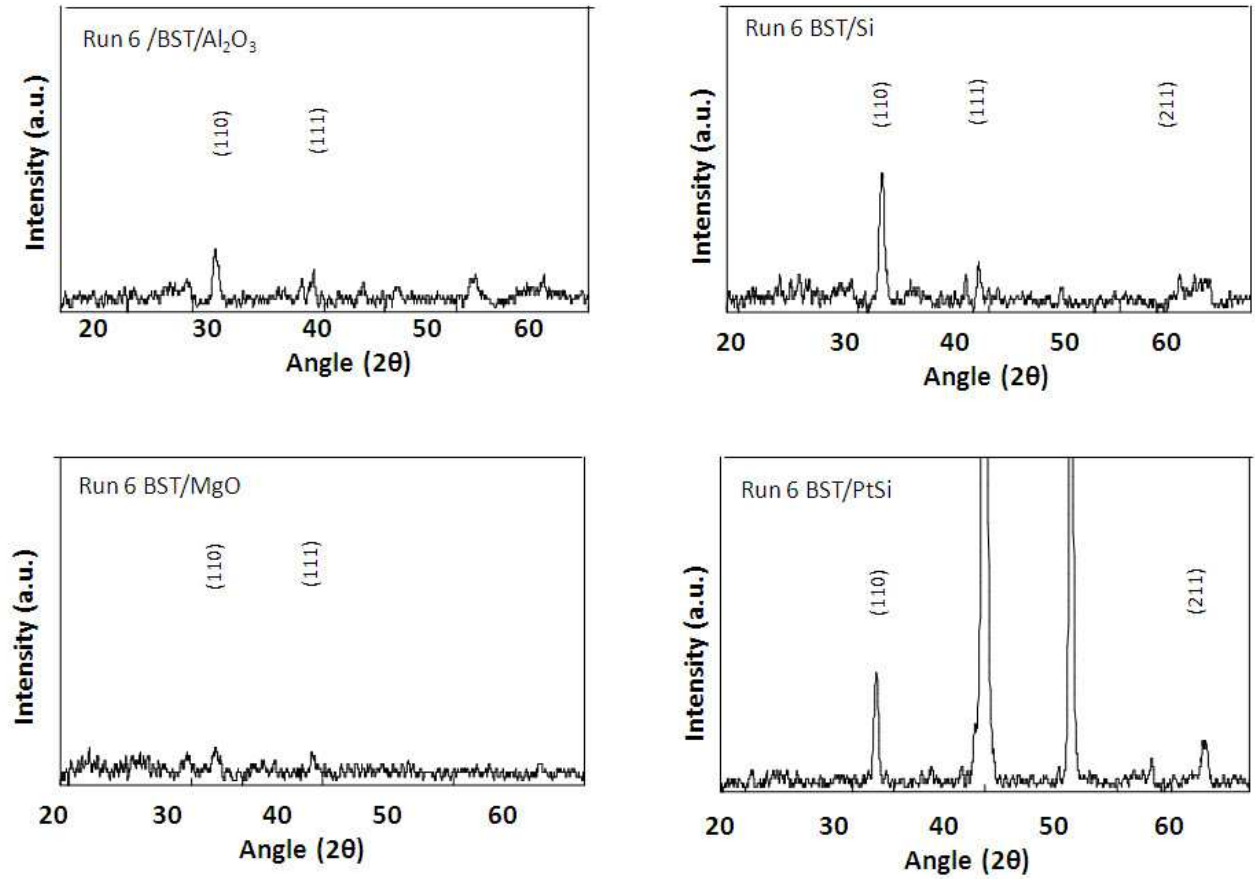
Figure 7: XRD spectra for BST films from a single growth run on each on Al_2O_3, Si, MgO, and Pt/Si (clockwise from top left). Note the two large unlabeled peaks on Si/Pt are from Pt.
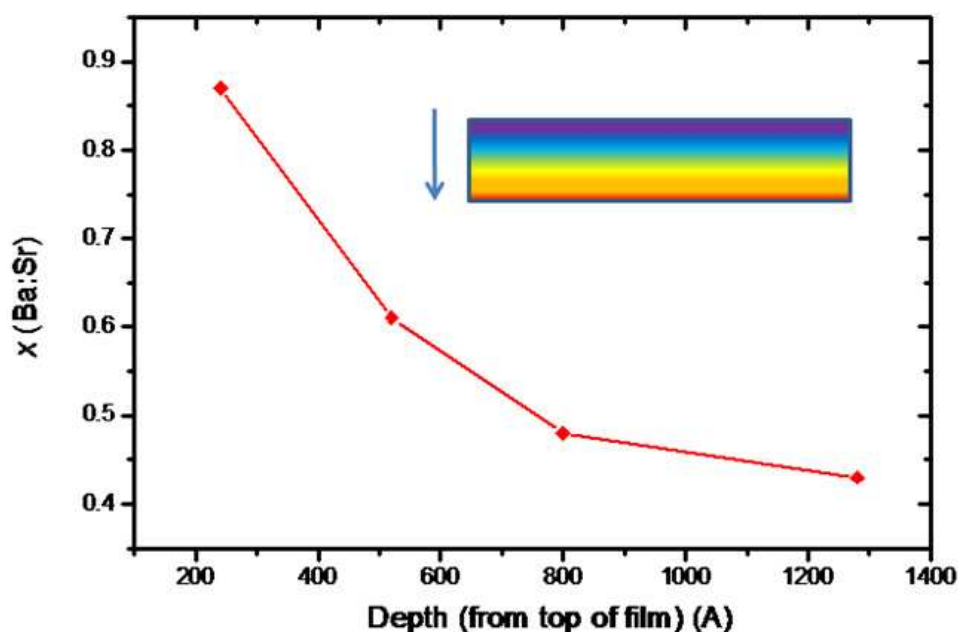
Figure 8: Depth profile plot of the ratio of Ba:Sr for a compositionally graded BST thin film on MgO.

the film with depth. RBS is an established, non-destructive analysis method for determining thin film composition. The technique measures scattering of incident high energy ions on the sample, and a key feature of RBS is the ability to provide composition depth profiles hundreds of nanometers without disturbing the sample, something that electron based methods cannot provide. A limitation of RBS is cost and availability. Unfortunately the RBS facilities at ARL had been off-line during this time, and we employed the services of a commercial analytical facility Evans Analytical Group (EAG).

Shown in Figure 8 are depth profile results from RBS analysis for the graded BST film on MgO. Plotted in this figure is the Ba:Sr ratio with depth (from the top of the film). The ratio of Ba to Sr was controlled from 0.87 to 0.43. The total film thickness is 130 nm. RBS spectra were taken at four (increasing) depths from the topmost surface. As is evident, the ratio changes are consistent with the growth steps described above. There was however was an excess of Ti in the films. This is not surprising since the Ti(thd) precursor has been found to be highly reactive. The relative amount of Ti in the precursor flux was reduced in subsequent runs and the film layer thickness were varied.

Having demonstrated the capability of RCC 2.0 for creating both constant composition and compositionally graded films, our efforts were then aimed at electrical testing of BST films. The first step was to optimize BST film films on platinum electrodes with Si and Al_2O_3 as the substrates. For comparison with ongoing work at ARL, we decided to begin with optimizing constant composition films of BST 60:40. With guidance from ARL, we deposited platinum electrodes on MgO substrates at Caltech by sputtering. However, it was found that ARL could produce much higher quality electrodes, and they graciously provided us with silicon and sapphire substrates with Pt bottom electrodes.

Near the end of the third year of this project, quality issues with the Ba and Sr metalorganic precursors from our longstanding supplier, SAFC Hitech Inc., were encountered. Although
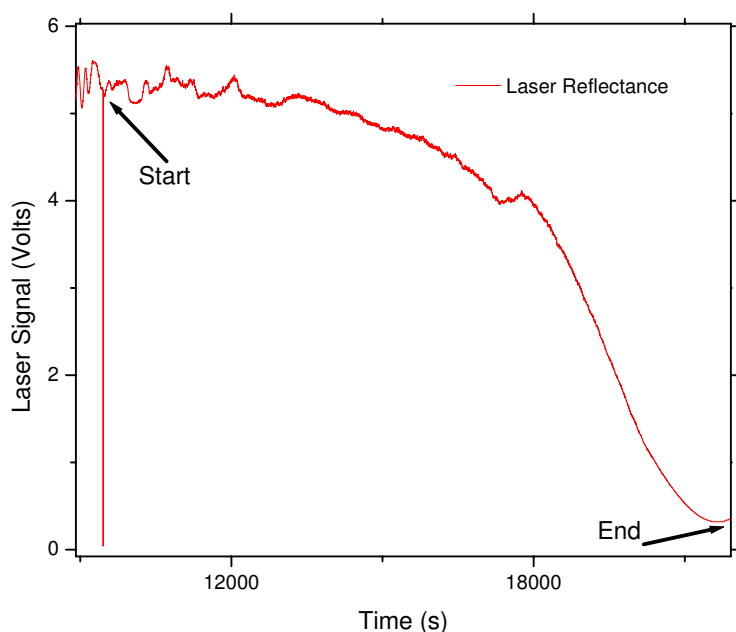
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Figure 9: Plot of reflected laser intensity with time during BST film growth. The film thickness was 85 nm and the growth time was 210 minutes.

these Ba and Sr precursors had worked well for many years, they stopped performing. In situ UV spectroscopy of the vaporized precursors showed a reduced volatility. This was consistent with the large amount of precursor remaining in the bubblers after growth. We worked with the vendor to understand these problems. We returned our batches of precursors to SAFC Hitech for examination. It was eventually determined that the company's only lots of Ba(thd) and Sr(thd) had degraded in storage over time at the company. Due to lack of demand, fresh batches had not been fabricated, and synthesis of new batch would be cost and time prohibitive. A new source for precursors was needed. However, there are only a few alternate suppliers.

This presented a serious setback. The growth parameters in the first part of this project had been tuned to the specific properties of the SAFC Hitech precursors. Products from other suppliers most likely would not perform in a similar manner. The growth process parameters would have to be redetermined.

To help rapidly assess the performance of the replacement precursors, a laser reflectometer was employed in the MOCVD reactor. This enabled instant monitoring of the film deposition rate (or not) in real time and allowed conditions to be adjusted accordingly. It also allowed us to determine the film thickness in situ. The reflectometer setup is simple; it consists of a HeNe laser and photo-diode detector. The laser is incident at 60 degrees from normal on the substrate and the beam is reflected from the sample into the detector. Changes in film thickness result in corresponding changes in the reflected laser intensity, and this can be monitored in real-time. For the purposes of these experiments, it was sufficient to determine the onset of film growth and the relative rate of film growth. Because this could be monitored instantly, the reflectance provided a very simple means for monitoring the effect of changing parameters such as flow rates and bubbler temperature.

We explored barium and strontium precursor products from SAFC Hitech and two new vendors, Strem Chemicals Inc., and Rare Earth Products Inc. For simplicity, film growth runs of barium oxide (BaO) were performed while monitoring the laser reflectance. SAFC Hitech provided Ba(thd) in phenanthroline, which is a new formulation of the older product that we had previously used. Although, it exhibited a large signal in UV, there was no evidence of film growth and almost no Ba found on the substrate by electron dispersion spectroscopy (EDS), which measures the atomic composition of the film.

The conventional forms of Ba(thd) were provided by Strem Inc and Rare Earth Materials Inc and tested. Both exhibited drops in the laser reflectance during growth indicating the formation of film. We also observed that both sets of precursor were apparently volatile as by evidenced by a strong UV absorption signal. However the maximum for this signal was shifted from that of the original SAFC Hitech. At the time, this was attributed to a manufacturing variation in the precursors. EDS showed that the both films contained barium, but the films from the Strem precursor contained the most barium.

Having selected the barium precursor from Strem, our attention was turned towards understanding its reactivity. To this end, we pursued growing $BaTiO_3$. This was done to compare the relative performance of the barium and the titanium precursors. Typically, the titanium precursor is much more reactive than either the strontium or the barium precursors. That being said, the relative molar flow amounts (moles/minute) delivered to the sample are typically not stoichiometric i.e. Ba:Ti 1:1, and the relative precursor flow compositions must be found empirically. Strontium behaves in a similar manner as barium, but from our previous experience it was found to be more reactive than barium.

$BaTiO_3$ (BT) and BaSrTiO3 (BST) films were attempted using previous ratios of Ba:Ti 10:1. We observed an apparently strong volatility via the in situ UV absorption of the bubbler effluent, but EDS showed almost a complete lack of Ba in the films. Our first thought was that there was a cold spot in the precursor delivery system. A cold spot is where there portion of the gas lines that is much colder than the bubbler temperature, and this causes the flowing precursor to condense in the line before reaching the sample. Typically, this is caused by a short in the electrical heating tape warming the lines. The gas lines were examined and several issues were found and corrected.

Additional growth runs were conducted; however there was still an absence of appreciable barium or strontium in the films. The films were mainly TiO_2. This was puzzling since we observed strong signals in the UV and there were no cold spots in the lines. It was then realized that perhaps there was an issue with the UV absorption. In particular, something related to the change in the UV absorption maximum that was observed during the initial testing of the precursors. The effective vapor pressure of the bubbler is dependent on the temperature, and the original precursors from SAFC HiTech provided suitable vapor pressures of Sr or Ba at 235 °C. Often times, however, a phantom UV signal was observed at lower temperatures during the heat up phase. It would eventually go away when the temperature was increased and the true signal was revealed. The phantom signal was regarded as an outgassing of a minor component of the precursor.

To overcome this, the bubbler temperatures were raised substantially. The temperature was increased by almost 35 °C, and the proper UV signals were finally restored. At this point we were able to run at substantially higher total mass flow rates of 2-4 μmole/min and observed film growth in situ via laser reflectance. We also observed molar flow rates above 2 μmole/min were necessary to maintain reasonable growth rates.

	% Flow	sccm	Ba:Sr	(Ba+Sr):Ti
Ti	0.04	75		
Ba	0.61	4575	0.4	0.9
Sr	0.35	1389		

Table 1: Table of flow conditions and resulting BST film compositions, as measured by EDS

Based on this revelation, a series of growth runs was undertaken with the Strem precursors to optimize conditions for the relative amounts of Ba:Sr and the total amounts of Ba and Sr to Ti (Ba+Sr):Ti. The film compositions were measured at Caltech by electron dispersive spectroscopy (EDS). The EDS results indicated a substantial excess of titanium in the films. This indicates that newer Sr and Ba precursors are much less reactive than our original batches from SAFC HiTech. The relative amount of titanium in the precursor flux was reduced from 22 to 4%. After the first few runs, we were able to get a film within an acceptable range. Shown in Table 1 are the flow conditions that gave us nominal BST 40:60. The average Ba:Sr was 0.4 and the average (Ba+Sr):Ti was 0.9.

The samples were sent to ARL for structural characterization. Shown in Figure 10 are SEM and AFM images of the SEM and AFM images of a BST film produced under these new flow conditions. The films are crystalline and are 85 nm thick. The growth is columnar, and there is good delineation between layers. The roughness, Ra, as measured by AFM is 4.8 nm. Shown in Figure 11 are XRD spectra of BST grown on platinized silicon and sapphire.

However, unlike our previous results, the majority of the film is BT (111). There is a smaller amounts of BST[60:40] (110) and off phases of ST. This was unexpected because composition analysis by EDS indicated stoichiometric amounts Ba and Sr. The hardware of the MOCVD system was examined for any anomalies. A slight blockage of the strontium precursor lines was discovered and resolved. A second series of runs was performed in the Fall 2011. However, similar results were obtained as the last series of runs. XRD showed that the films were primarily crystalline BT. Having only crystalline BT, while there is elemental Sr in the films indicates a problem with the reactivity of the strontium precursor.

IV   ARL collaboration

Over the course of this project we have maintained an ongoing and fruitful collaboration with Dr. Melanie Cole, Leader of the Active Materials Group at ARL-WMRD. There have been numerous"face-to-face" meetings and regular telecons over the course of the project. A highlight of this collaboration is joint authorship on two papers. There was a site-visit by Dr. Boyd to ARL to meet with ARL scientists in 2011. This collaboration has involved technology transfer, software development, and sample characterization and process development.

A major accomplishment of the ARL-Caltech collaboration is the transfer of MOCVD technology from Caltech to ARL. Dr. Cole is establishing MOCVD capability within her group at ARL-WMRD, and she selected to build an expanded system based on the Caltech MOCVD technology. Caltech worked closely with ARL personnel to transition and adapt the unique MOCVD technology to the ARL reactor system. This included working extensively with ARL to realize the reactor hardware design architecture of their system as well as growth processing methodologies. Shown in Figure 12 is an image of the completed ARL reactor.
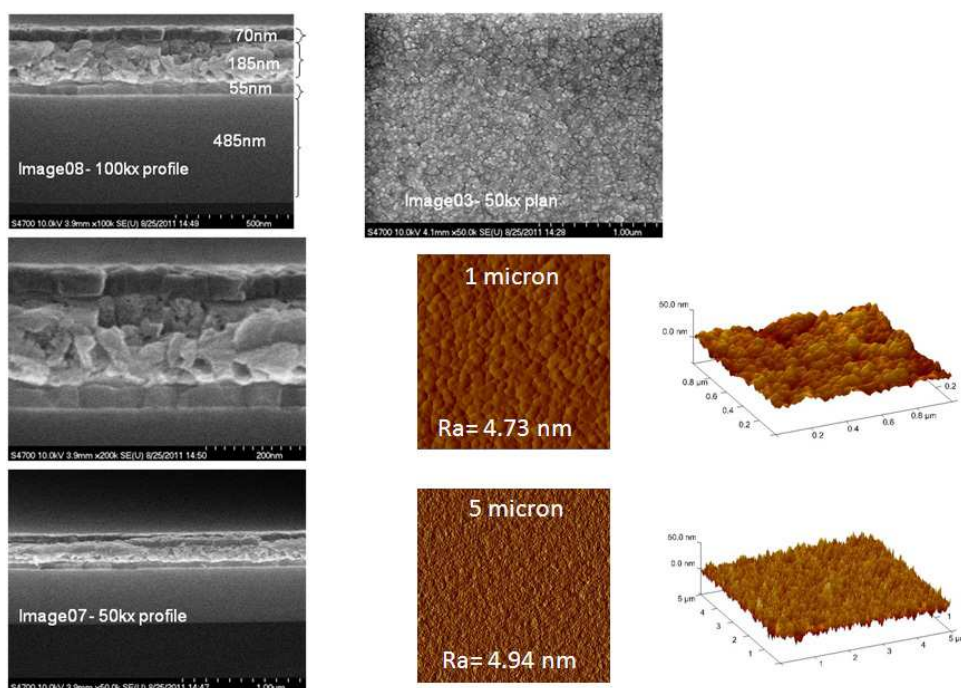
Figure 10: SEM and AFM images of a BST produced under the new flow conditions. The film is 85 nm thick. The growth is columnar, and there is good delineation between layers.

An important part of the collaboration with ARL included development of the reactor control software, RCC 2.0. The RCC is a key component of the MOCVD system. The software control and monitors all parameters of the film growth and enables the growth of complex oxide heterostructures. The RCC 2.0 software was first developed, tested, and optimized at Caltech with support from ARL. The software was then transitioned to ARL-WMRD, whereby it was been modified to accommodate the additional complexity (additional bubbler cell and more extensive growth controls) of the ARL system.

Currently, the ARL reactor is in operation and has begun MOCVD growth runs. Caltech has worked with ARL scientists to transfer technical knowledge including hardware setpoints, methodologies, and precursor selection and characterization. There was a site visit by David A. Boyd of Caltech to ARL in the Fall of 2011. Dr. Boyd met with ARL scientists to view the finalized reactor system and discuss growth methodologies and process development.

ARL assisted Caltech in film characterization and substrate preparation. Structure-process-property correlations were developed, and this direct feedback enabled the MOCVD growth optimization at Caltech. A shared data-base has been established between Caltech and ARL-WMRD in order to support and sustain collaborative data import and export. This included metalorganic precursor performance, growth parameters, and specific MOCVD methodologies for BST thin films. ARL has provided bottom electrode samples as well as guidance in creating bottom electrodes.

V   Summary of Results

An advanced reactor control code, RCC 2.0, was developed for the growth of complex MOCVD thin film structures in collaboration and support with ARL. The RCC 2.0 software was used
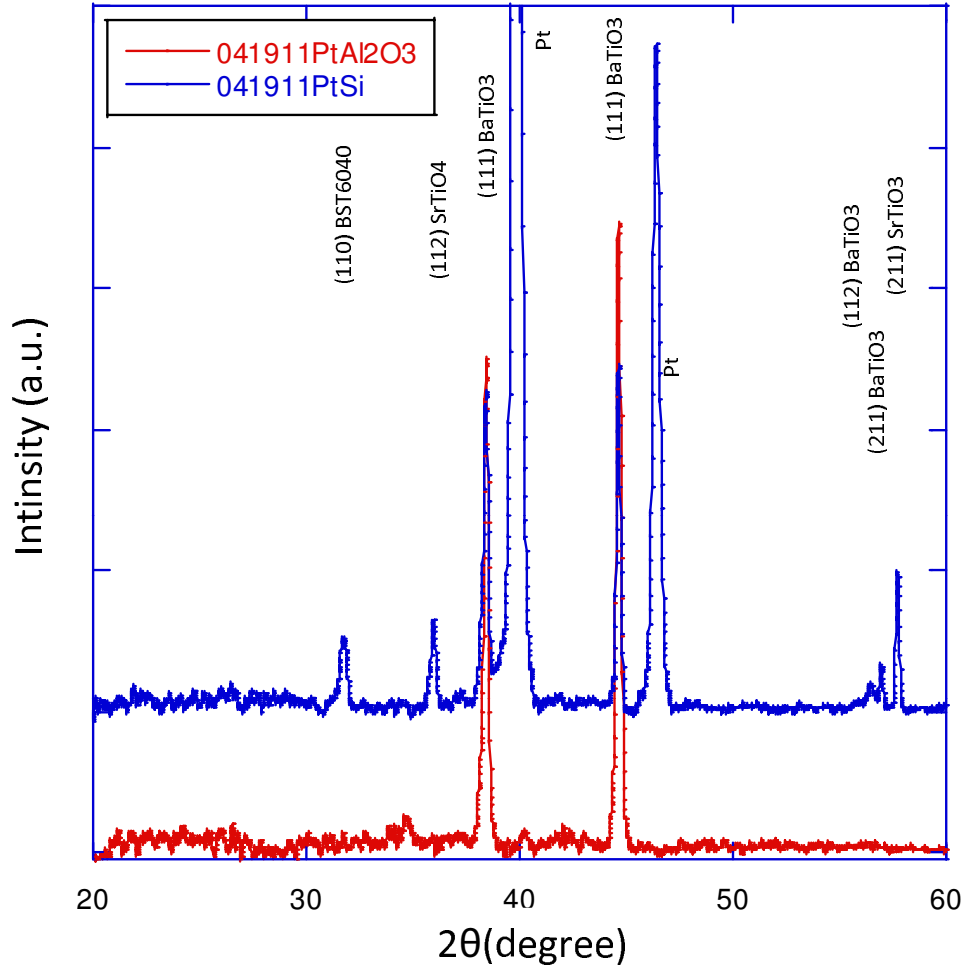
Figure 11: XRD spectra of BST grown on platinized silicon and sapphire. The films are crystalline. The majority of the film is BT (111).

Figure 12: The ARL MOCVD reactor. Caltech and ARL worked together to transition MOCVD reactor technology from Caltech to ARL. The reactor design was based on the Caltech MOCVD reactor and was modified accordingly for additional complexity required by ARL. The reactor control software was developed jointly.

to develop process and growth parameters for MOCVD growth of BST. Crystalline BST thin films were grown over a range of desirable Ba:Sr ratios on a MgO, Al_2O_3, and Si, and Si/Pt substrates.[1] Using these results from these constant composition studies, compositionally graded BST thin films were successfully deposited.[2]

Subsequent film growth studies encountered issues with the quality of metalorganic precursors provided by a long-term supplier. This required evaluating and selecting new batches of precursors from different vendors. During this process, a simple, in situ, laser-based technique was developed to measure the film growth rate and film thickness. The behaviors of the new precursors were found to substantially different from the original ones, and the growth process parameters for BST had to be re-determined through additional series of growth runs. Films from the newer batches of precursors were found to be crystalline and contained BST (60:40), which was the target composition, but the majority component was crystalline BT. Although EDS measurements showed stoichiometric amounts of elemental barium, strontium, and titanium in the films, it was determined that the particular strontium precursor, which was sufficiently volatile, was apparently not reactive enough to completely form BST (60:40) throughout the film.

Caltech and ARL collaborated extensively over the course of this project. Caltech MOCVD reactor and system technology was transferred from Caltech to ARL. ARL supported development of reactor control software at Caltech; this software was then transferred to the ARL MOCVD reactor. The ARL reactor is currently in operation. ARL assisted in film characterization and provided platinized substrates for film BST growth. Caltech and ARL developed a shared database of process parameters, film properties, and metal organic precursor properties.

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